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THE EFFECT OF THE MEDIUM AND OF ADSORPTION LAYERS ON PLASTIC FLOW OF METALS

P. A. Rebinder and Ye. K. Venstrem

ABSTRACT. It is demonstrated that the plastic flow of metals (tin, lead and copper) before rupture and plastic rupture are considerably facilitated (accelerated) by introduction to the nonpolar (hydrocarbon) liquid (pure vaseline oil) in which the experiments are performed of small quantities of surface active materials. The dependence of this effect on the concentration of the surfactants is investigated in detail. It is shown that the greatest effect is achieved at concentrations corresponding to complete saturation of a monomolecular adsorption layer. At high concentrations, the effect decreases once more. The relationship of these phenomena to the facilitation of brittle rupture (dispersion) of solid bodies under the influence of adsorbed materials and to the "cleaving influence" of thin liquid layers is established. The significance of this effect of "internal lubrication" in the effect of lubricating-cooling fluids during metal working by pressure and by cutting is indicated.

Introduction

In many works of our laboratory, beginning in 1927 [4], it has been shown /531[1] that small additives of adsorbed material to the surrounding medium can significantly reduce the strength of solid bodies in the medium for brittle rupture. This phenomenon of "adsorption reduction of brittle strength" has been investigated in our laboratory both as applicable to elementary rupture, in the rupture or splitting of crystals (calcite, mica), and as applicable to summary ruptures, in the dispersion of solid bodies (such as in processes of grinding, drilling, cutting and polishing).

In our studies, we have discovered and investigated the effects of small additives of adsorbed materials of reducing both the rupture strength, i.e. the rupture stress and the work of dispersion, i.e. the work required in a given dispersion process to form a new unit of surface area of the solid body at the boundary with the surrounding medium. This last quantity, $H = dA/ds$, which we have defined as the hardness, is an analog to the specific free surface energy /532 of a solid body (σ), and can be used to conveniently characterize the behavior of the body in question in the dispersion process used, by expressing it as its

[1] Numbers in the margin indicate pagination in the foreign text.

inverse quantity, the workability of the body:

$$\frac{1}{H} = \frac{ds}{dA} \text{ or } \frac{dv}{dA} = \frac{1}{H \cdot \beta},$$

where $\beta = ds/dv$ is the degree of dispersion, i.e. the specific surface of the dispersion product, ds is the newly formed surface, dv is the dispersed volume of the body. Due to the irreversibility of rupture processes (and dispersion processes) in most cases H is many times greater in absolute value than σ; however, as our work has shown, $H = dA/ds$ is roughly proportional to the specific free surface energy, which determines the intensity of the molecular forces acting in the body: $H \simeq k\sigma$, where $k \simeq H/\sigma$ is a quantity which is roughly constant for bodies of various hardnesses in a given dispersion process, the "coefficient of irreversibility" of the process, the inverse of the efficiency, $1/k \simeq \sigma/H$. In the particular case of an ideal dispersion process, i.e., reversible formation of a new surface of the solid, for example splitting of mica along cleavage planes, $k \simeq 1$, and the hardness in our definition corresponds to the specific free surface energy, which V. D. Kuznetsov used as a measure of the hardness for brittle dispersion [3].

In our very first works on the problem of reducing strength (hardness) by the influence of adsorbed additives introduced into the surrounding medium, we showed [11] two possible factors causing this effect and obviously acting in tandem.

1) Facilitation of the formation (birth) of surface fissures in the solid body when subjected to a given mechanical effect, under the influence of the formation of adsorption layers on its external surface due to the involvement of the molecular forces binding the surface atoms of the solid body with the adsorption of molecules from the surrounding medium. Due to this, microfissures may be generated in the surface of a solid at lower stress levels. The formation of such seed fissures may considerably reduce the strength of a specimen within its three-dimensional volume as well, due to concentration of stresses in the fissures in correspondence with the theory developed by Griffiths [9] and the concepts of A. F. Ioffe [10] concerning the great reduction in strength under the influence of surface fissure defects on the surface of a specimen.

2) As a result of its penetration into the body through the microfissures formed and developed beginning at the surface of the specimen being dispersed, the adsorbed material, forming adsorption layers in these fissures in the interior of the body (in the mouths of the broader portions of the fissures), would reduce the work required to form these fissures $dA \simeq k\sigma ds$, decreasing the free surface energy σ on the "internal" surface. In recent times, the works of B. V. Deryagin and his colleagues [2] have shown that the mechanism of facilitation of the development of fissures under the influence of a liquid medium penetrating into them may be related to the "splitting" effect of thin films of liquids between solid surfaces. This splitting effect, noticeable with film thicknesses of 0.1 μ, increases sharply with a decrease in the thickness and

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results from the formation of diffuse solvate shells -- transition layers of liquids bonded to the surface of the solid body. In order to press out the solvate shells, which have primary significance in the lubricating effect according to the concepts of B. V. Deryagin, high pressure must be used, exceeding the cleavage pressure. After forming in the fissures, these transitional solvate liquid layers actually split the solid body along these fissures, facilitating the development of fissures in the areas into which these layers penetrate, and extending further into the depth of the fissures as they expand. The molecular cleaving action of the medium in the fissures consequently cooperates with the mechanical effect of the bursting stresses during rupture. The concept of the splitting effect only explains the significance of the decrease in free surface energy in the facilitation of rupture (formation of fissures), pointing out the corresponding molecular-force mechanism. Actually, the solvate transition layers of the surrounding medium at the surface of a solid body are more strongly expressed, and their splitting effect is stronger, the more lyophilic the division surface is, i.e. the more strongly σ is reduced [5].

The considerable facilitation of brittle rupture (dispersion) under the influence of small additives of adsorbed materials to the medium surrounding the solid body is related to the increase in the splitting effect in the formation of an adsorption layer on the surface of the solid. According to Deryagin, we can think of this effect either as an increase in the thickness of the solvate shell in the transition layer between the solid surfaces in the fissure or as a corresponding increase in the splitting pressure with constant film thickness. This effect can be quite considerable, since we have already shown that covering a surface with a monomolecular adsorption layer can sharply change its molecular nature, for example considerably increasing the affinity of the surface for the surrounding medium, which is quantitatively and quite clearly expressed in wetting phenomena, as well as in the stabilization of dispersed systems.

In work performed in our laboratory on detailed investigation of the /534
facilitation of brittle fracture under the influence of the medium toward which the solid body in question is most lyophilic, i.e., has the greatest decrease in σ, as well as under the influence of adsorbed active material additives, we have investigated the decrease in strength during splitting along cleavage planes of calcite crystals (N. Ye. Markova) and mica crystals (G. I. Logginov). It was found that with sufficiently slow increase in the cleaving force to the critical value, this force can be approximately halved under the influence of adsorbed additives in the surrounding medium (water), even for crystals of significant size (1-2 mm). The effect is considerably strengthened if the specimen is held for a rather long time in the stressed state (several hours or even days) in a given medium (solution) (although at forces not exceeding the ultimate strength) [5]. The strongest influence of this extended action is achieved at the solution concentration (corresponding to the formation of a monomolecular adsorption layer) which gives the strongest effect without preliminary holding. These results, it seems to us, confirm beyond doubt our assumption of the penetration of the active adsorbed materials (additives) within the body along fissures which are developed beginning at the surface of

the body.

In the laboratory of A. F. Ioffe, our work on the influence of adsorption on strength has been recently used by S. N. Zhurkov to explain the influence of surface fissures (defects) and the condition of the surface on the strength of solids, small diameter specimens, the strength of which is considerably greater than that of ordinary specimens. S. N. Zhurkov [1], in his investigations of the tensile strength of very fine glass and quartz filaments (diameters to 3 μ) has found a considerable decrease in strength upon adsorption of water vapor, and also, to a lesser extent, upon adsorption of vapors of alcohol and benzene in comparison to the strength in a vacuum. It can be considered that the adsorption of vapors in these experiments was accompanied by condensation of the vapors on the surface of the filament and particularly in the surface fissures which appear before rupture. Thus, it can be considered that the results produced correspond to rupture in pure liquids of various polarities. These results correspond completely to the general theoretical position which we have stated before [4]: the liquid in which a solid body to be ruptured is contained decreases its strength in comparison to its strength in a vacuum or in dry air more strongly, the more similar the polarity (molecular nature) of the liquid to the polarity of the solid, i.e., the less the difference in polarities or specific free surface energies σ at their common boundary.

Thus, glass or quartz, being hydrophilic, highly polar bodies, show the greatest decrease in polarity under the influence of water, and this decrease is /535 gradually reduced as water is replaced by less polar liquids. On the other hand, the decrease in strength of hydrophobic (oleophilic), i.e. nonpolar solids such as coal or graphite resulting from the influence of the surrounding medium, increases with a decrease in polarity of the liquid, i.e. for example upon transition from water to heptane (kerosene). This was proven by our measurements of the dispersability of graphite during polishing, as well as certain experiments on the grinding of solids in various liquids using ball mills, conducted at the Institute for Mechanical Processing of Minerals (Mekhanobr). These general considerations agree fully also with the concepts of the splitting effect: the formation and further development of surface fissures in a solid body is facilitated more, the lower the specific free surface energy at the boundary of a body with the surrounding medium, that is, the firmer and thicker the solvate shell -- the transition layer of the liquid formed between the two surfaces of the solid body causing splitting along fissures.

N. M. Krasovskiy in our laboratory, during an investigation of the influence of adsorption layers, formed by adsorbed materials from solutions in water and nonpolar hydrocarbon liquids on the tensile strength of quartz and glass fibers of various thicknesses, showed that a considerable decrease in strength is also observed during the rupture of thick filaments 100 μ and more in diameter. This agrees fully with our measurements on the splitting of calcite crystals and confirms the significance of penetration of the materials into surface fissures.

In connection with our investigations of the facilitation of brittle rupture of solid bodies under the influence of adsorption layers, it seemed to

us quite interesting to investigate the possible influence of these same adsorption layers, formed by small additions of surface active agents to the surrounding medium, on plastic flow of bodies and in particular of metals, monocrystals and polycrystalline samples. This influence, with sufficiently slow plastic flow of metals without rupture, should be of great practical significance in investigations of the phenomena of creep, wear, the lubricating effect, particularly during the processing of metals by pressure and during polishing. The investigation of this possible influence of the composition of the medium and additives to the medium on phenomena of plastic rupture of metals is of great significance in the study of processes of cutting and the influence of lubricating and cooling fluids on the cutting of metals.

The phenomenon of plastic deformation of metals must be looked upon as internal dispersion of the specimen, i.e., as the formation of internal division boundaries within the metal along slipping planes or as a result of rotation of some sectors of the crystalline lattice in relation to others. These phenomena /536
of internal dispersion in polycrystalline samples during plastic deformation, also observed in monocrystals, are complicated by displacements along intercrystalline boundaries. Thus, in contrast to elastic deformation, plastic deformation must be looked upon as unique, nonterminating internal ruptures, which are transformed when deformation is increased, for example during metal flow, into clear plastic rupture.

The internal dispersion which occurs during plastic deformation appears on the surface of a specimen in the form of a system of irregularities -- fissures, traces of slipping planes (luders lines). The surrounding medium and active adsorbed additives included in it can penetrate into the specimen to a certain depth along these fissure irregularities, as well as along the intercrystalline boundaries. It can be expected that this will result in a considerable increase in the flow rate even of rather thick metal samples, as well as facilitation of plastic rupture.

Experimental Portion

In our experiments, we investigated the flow of tin, lead and copper. Tin (highly pure, imported) was used in the form of rather thick foil; strips 75 mm long and 3-10 mm wide were cut from homogeneous sheets of the foil about 0.06-0.07 mm thick. In many cases, these strips were annealed to remove residual changes arising in the cutting operation before measurements were performed. This annealing caused no significant changes in the final results. The lead (pure, from Kal'baum) was tested in the form of foil strips 70 × 6 × 0.035 mm, as well as in the form of round cross section wire 0.5-1.0 mm in diameter which we produced by drawing through the apertures in a steel drawing plate (with constant decrease in diameter upon transition from one aperture to another). In this case also, the lead wire produced was annealed for some of the experiments. The drawing operation produced wire with a completely smooth surface, and sectors were selected for measurement with no noticeable "macro"-damage to the surface. The copper (electrolytic) was selected in the form of 0.1-mm-diameter wire. All the wire was preliminarily annealed in a vacuum. During the plastic

flow measurements, the samples were located horizontally or vertically (see the diagram on Figure 1a, 1b), one end of the sample being carefully clamped in a nonmoving clamp a, while the other end was held in the free, light clamp a' made of aluminum, to which a thread was connected which passed through block S and carried constant load P, which created the tensile force. The experiment was performed in the liquid medium being tested, which was poured into the flat aluminum trough L, the top of which was closed by a glass plate ground to fit the edges, in order to prevent evaporation of the solution or, in the vertical position (b) in test tube K. In all our experiments we carefully avoided /537
additional resistance due to friction of the solid surfaces: movable clamp a' did not touch the bottom of the trough, and the thread fastened to it passed freely through the aperture in the aluminum wall. The block was set up so that the application of the force was straight along the axis of the specimen. The initial length of the specimen between the two clamps (about 70-80 mm), as well as the elongation of the specimen due to flow, were measured using a comparator or horizontal cathetometer M with readings down to 0.02 mm. Observations of elongation were continued with a given P = const right up to rupture. In addition to these detailed measurements, in which the entire kinetics of the flow of the loaded sample were investigated to rupture, for each medium (solution of a given concentration) and each metal, a large number of secondary experiments were performed in which only the time of total flow to rupture and the limiting (critical) elongation of the sample at rupture were determined. These latter experiments were also performed for extremely slow flow, under conditions of so-called creep of the metal with low stress, when the time of flow to rupture varied from several hours to a full day or more. Investigations were performed at constant temperature, for example in a thermostat.
L. P. Yanova in our laboratory investigated the influence of the medium or surface active additives on the flow of metal at high temperatures. In order to do this, the bath containing the liquid being investigated in the sample was placed in a horizontal electric furnace. For measurements in the area of low /538
temperatures, the specimen was stretched vertically in a glass tube placed in a Dewar flask with the cooling medium. The results of the investigation of flow at various temperatures will be reported in a separate article. Here we present only data from measurements made at room temperature (about 20°). In many control experiments, particularly those performed with nonvolatile liquids (vaseline oil) and solutions of nonvolatile active agents in these oils, the flow of the specimen did not begin in the vertical position immediately upon placement of the specimen in the liquid, but rather only after abundant wetting of the entire surface of the specimen with the liquid, with the specimen suspended freely in air.

Due to the unsatisfactory reproduceability of individual results, all measurements were repeated many times, so that the final results presented in Figures 3-8 are averages from many tests.

The vaseline oil used as the medium for most of our experiments was of the highest purity and contained no polar additives. It was purified to remove the last traces of these impurities and dried by holding over pieces of metallic sodium freshly cut from the surface. The shiny surface of the sodium did not change at all, even after long exposure to this oil. The oil was stored away

from air, and the experiments were always performed with fresh portions of oil. The vaseline oil was tested by us for purity by measuring the surface tension at the boundary with water and aqueous solutions of alkali (NaOH, Na_2CO_3) in a device used in our laboratory, using the method of greatest drop formation pressure (at the oil/water boundary). Thoroughly purified vaseline oil always showed the highest value of surface tension at the boundary with water (at 20°, σ_{12} = 52 erg/cm^2) near the value for saturated hydrocarbons (paraffins C_nH_{2n+2}). Also, this value did not change, i.e., did not decrease noticeably, when the aqueous phase was alkalized. The surface active agents, used in the form of additives to the solutions in vaseline oil, were received from Kal'-vaum. We investigated fatty acids of the normal series: valeric acid, heptylic acid, stearic acid, oleic acid, cerotinic acid, cetylic acid (see table below), as well as other surfactants (phenols, amines, etc.). However, the results produced from the latter, like the results of investigations of plastic flow in aqueous media, will be presented in another article to be published later.

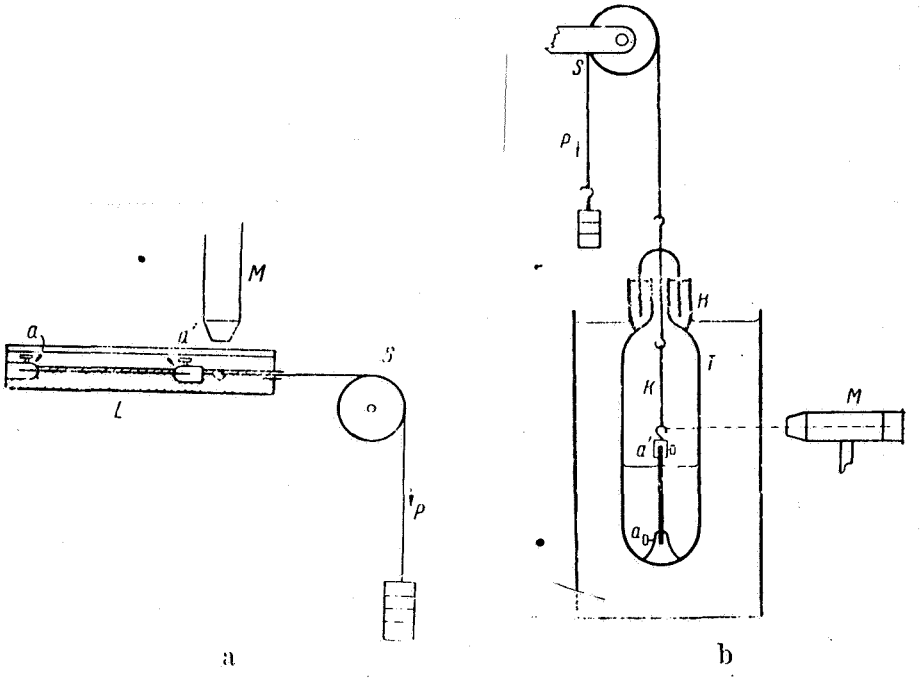

Figure 1. Diagram of Installation for Investigation of Plastic Flow of Metals in Various Media

Results of Measurements

All of our measurements, in complete agreement with the assumptions stated on the basis of our work on the facilitation of dispersion by adsorbed additives, indicate that surfactants added to a polar medium consisting of pure

vaseline oil, or kerosene, can considerably increase the rate of plastic flow of metal and facilitate plastic rupture. The introduction of such additives of surface active agents with a polar group in the molecule and a sufficiently long hydrocarbon chain to a purely hydrocarbon, nonpolar medium (liquid) causes: 1) a decrease in the time of flow of a specimen to rupture τ_p with constant stress; 2) a decrease in the critical force P_τ resulting in rupture of the specimen over a fixed period of time τ - const; and for lead also 3) a decrease in the critical (greatest) elongation $100(\Delta l_k/l_0) = 100\,\epsilon k$ at rupture; in the case of tin, this quantity remains constant, almost independent of the composition of the medium ($100\,\epsilon_k \simeq$ 35-40%). On the other hand, the rate of plastic flow of the metal $v = d\epsilon/d\tau$ or $dl/d\tau$ increases considerably more sharply under the influence of surfactants for tin than for lead. /539

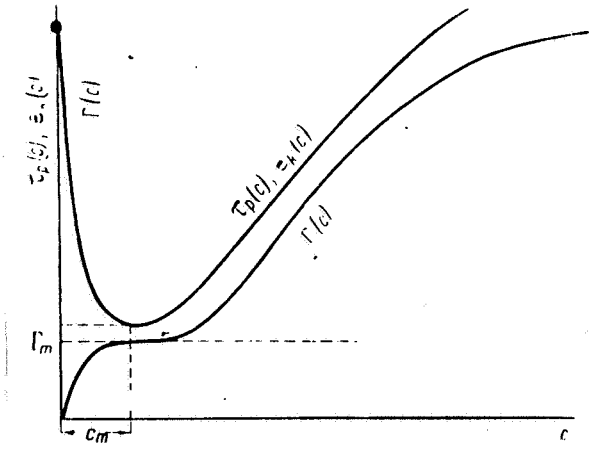

Figure 2. Diagram of Dependence of Flow Time to Rupture $\tau_p = f(c)$ or Greatest Elongation $\epsilon_k = \theta(c)$ on Concentration c of Surface Active Agent in Vaseline Oil in Parallel to Adsorption Isotherm $\Gamma = \Gamma(c)$

Our experiments produced broad material to explain the influence of the concentrations of surfactants added to the surrounding medium on all of these quantities. These concentration dependences, isotherms of plastic flow of the metal

$$\tau_p = f(c),\ P_\tau = \varphi(c),\ \varepsilon_k = \theta(c)$$

have a common form and are compared on the schematic drawing (Figure 2) with the isotherm of adsorption of the surfactant added at the division boundary between the metal and hydrocarbon medium. Figure 2, as well as Figures 3-8, which show the results of our measurements, show us that at very low concentrations, the flow time to rupture τ_p with constant force P or -- for lead -- the greatest elongation ϵ_k decrease sharply and almost linearly with concentration. This corresponds to gradual saturation of the adsorption layer according to the adsorption isotherm $\Gamma = \Gamma(C)$ (Figure 2). Complete saturation of the surfaces of the metal with the adsorbed molecules in a monomolecular layer, i.e., the least area in this layer per polar group always corresponds to the maximum effect of the additive, i.e., the greatest reduction in time to rupture or critical elongation. Apparently in all cases adsorption continues, and after a characteristic bend on the isotherm of adsorption, further increases in the concentration of the surfactant added result in the formation of a thick (polymolecular) adsorption layer. In the areas where this polymolecular layer /540

is formed, the effect of facilitation of plastic flow and rupture begins to decrease once agin with increasing concentration of the surfactant. The values of τ_p and ϵ_k increase once more, reaching almost their initial (greatest) values, corresponding to pure vaseline oil. It is interesting that this form of plastic rupture isotherm is apparently rather common; it corresponds to the form of the curves showing the dependence of the coefficient of external friction of two surfaces of the same metal on the concentration of the surfactant used to lubricate the boundary in a vaseline oil lubricant (lubrication effect isotherm). Also, concentration c_m, corresponding to the maximum effect, i.e., the minimum of τ and ϵ, depends primarily not on the nature of the metal (it is almost identical for lead, copper and tin) nor on the polar group in the molecule of the surfactant, but rather on the length of the hydrocarbon chain of the molecule, i.e., on the surface activity, the position in the homological series, in correspondence with Traub's rule. The concentration corresponding to the optimum effect, which matches saturation of the adsorption layer, decreases sharply with an increase in the length of the hydrocarbon chain of the surface active molecule, as we can see from the table presented below. At the same time, the effect, determined, for example, by the maximum decrease in flow time to rupture under the influence of the surfactant $\alpha = \tau_0/\tau_{c_m}$, also increases sharply with an increase in the length of the hydrocarbon chain. For example, stearic and oleic acids or cetyl alcohol produce a reduction in flow time to rupture at the maximum effect, i.e., when added to the vaseline oil in concentrations of 0.1-0.2% of α = 4-10 times, while cerotinic acid (see table in Figure 6) produces a maximum effect of reduction of τ_p for lead of α = 30-60 times at $c_m \simeq 0.001\%$.

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Surface active agent	Carbon atoms in chain	Most effective concentration	
		Percent	Millimole/liter
n-valeric acid C_4H_9COOH on lead	4	1.3	127
n-heptylic acid $C_6H_{13}COOH$ on lead	6	1-1.5	76-115
cetyl alcohol $C_{16}H_{33}OH$ on lead and tin	16	0.3	12
stearic acid $C_{17}H_{35}COOH$ on lead, tin and copper	17	0.2	7.0
oleic acid $C_{17}H_{33}COOH$ on lead and tin	17 (double bond)	0.1-0.2	3.5-7.0
cerotinic acid $C_{25}H_{51}COOH$ on lead	26	0.001-0.005	0.025-0.13

The table shows the concentrations corresponding to the greatest facilitation of plastic flow of metals for solutions of surface active agents in vaseline oil (see Figure 3).

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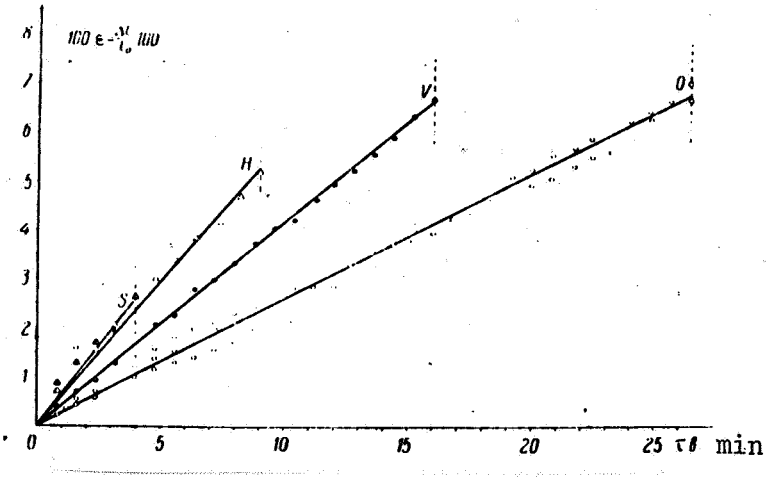

Figure 3. Kinetics of Plastic Flow of Bands of Lead Foil in the Area of Even Flow ($d\epsilon/d\tau$ = V = const, $100\ \epsilon = \Delta l/l_0 \cdot 100$). O, Kinetics of elongation in pure vaseline oil; V, With optimal addition (c_m) of n-valeric acid; H, Same for addition of heptylic acid; S, Same for addition of stearic acid. Optimal concentrations indicated in the table. Flow occurs at constant load P = 250 g

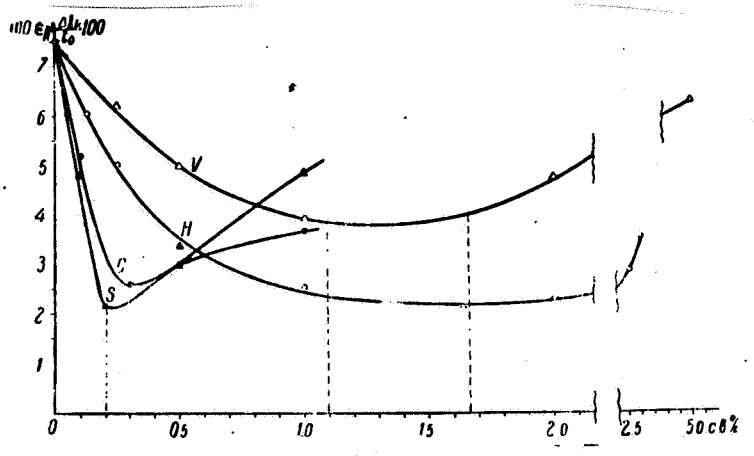

Figure 4. Isotherms of Greatest Elongation (to rupture) $100\ \epsilon_k = 100(\Delta l/l_0)_k$ of Strips of Lead Foil As a Function of Concentration of Surfactant Additive to Vaseline Oil: V, n-valeric acid; H, n-heptylic acid; S, Stearic acid; C, Cetyl alcohol

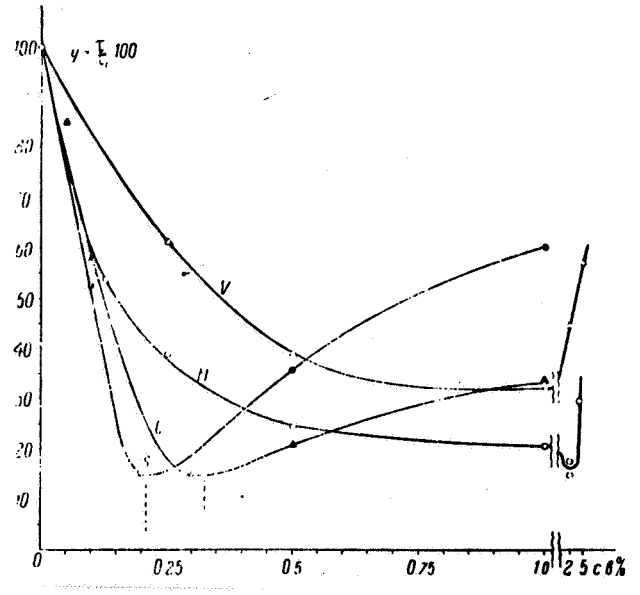

Figure 5. Isotherms of Relative Flow Time of Lead to Rupture $y = \tau/\tau_0 \cdot 100 = y(c)$ at Constant Load P = 250 g As a Function of Concentration c of Surfactant in Vaseline Oil; flow time of samples to rupture in pure vaseline oil always taken as 100. Symbols same as on Figure 4.

We have already indicated that the surrounding medium and the dispersing agents added to it can penetrate to a certain definite depth along fissure irregularities, thus facilitating further expansion of the fissures, i.e., flow and rupture of the metal. As was shown by A. V. Stepanov [10] in the laboratory of A. F. Ioffe, the presence of fissures in the surface layer actually does facilitate plastic deformation.

The effect which we investigated can, as with brittle factor, be looked upon (in the light of the works by B. V. Deryagin) as the splitting effect, at least in the initial portions of fissures at the external surface of the sample, as internal lubrication, completely analogous to ordinary lubrication by adsorption layers during external friction. Actually, our measurements of the coefficient of friction in solutions of surfactants in water and oil showed that the greatest effect, as was the case for the dispersing effect and the facilitation of plastic deformation of metal, was achieved at a concentration of surfactant corresponding to saturation of an adsorption layer (for example for oleic and stearic acids 0.1-0.2%). A further increase in concentration once more causes a reduction in the effect, as was found in our work on stabilization of suspensions in hydrocarbon media [12]. This corresponds to the concepts of B. V. Deryagin concerning the thickness of the solvate transition layers as a

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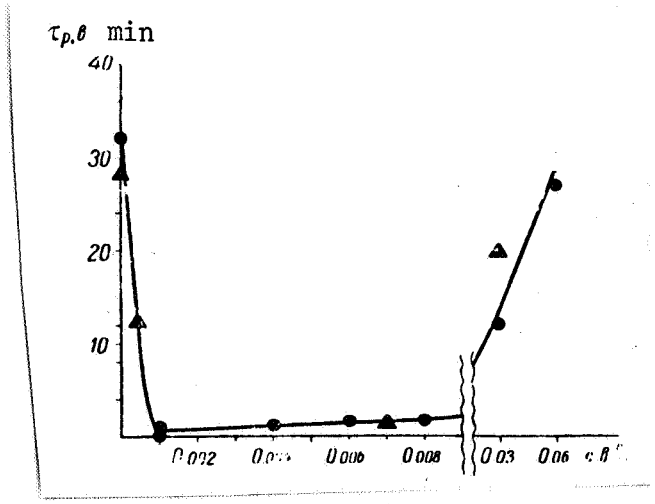

Figure 6. Flow Time to Rupture τ_p at Constant Load P = 300 g As a Function of Concentration c of Cerotinic Acid $CH_3(CH_2)_{24}COOH$ in Vaseline Oil for Strips of Lead Foil. Circles and triangles correspond to two series of experiments.

c.....	0	0.001	0.004	0.006—0.008	0.03	0.06%
τ_p..	28—32,	1—0,5	1	2	12—20	27 min

decisive factor in these phenomena in the sense of the splitting effect. Actually, complete orientation of the hydrocarbon chains perpendicular to the surface in the saturated adsorption monolayer corresponds to the greatest growth of solvate shells from the hydrocarbon molecules of the surrounding medium on these chains (see Figure 8). These saturated adsorption layers with long hydrocarbon chains of molecules turned toward the surrounding nonpolar medium can be looked upon in relation to the medium as unique, two-dimensional crystallization seeds. As a result of the orienting effect of such a seed and the influence of thermal movement on the surface which tends to disrupt this effect, a diffuse solvate shell is formed. At high concentrations, thick polymolecular adsorption layers are formed (see Figure 3); in these shells, the molecules are obviously bound to each other by their polar groups into colloidal particles. These layers no longer form the outward turned "bristles" of oriented hydrocarbon chains, and therefore do not bind the thick, strong solvate shells. This is also proved by the fact that the wetability of the surface for water [6], which reaches a minimum at the level of complete saturation of the monomolecular adsorption layer, increases once more with a further increase in the concentration and adsorption (upon transition to thicker layers).

Thus, the dependence of the coefficient of external friction on the concentration of the active "lubricating" material has the same form as the dependence of flow time to rupture on concentration ("internal lubricating effect").

Our measurements of the adherence of metal surfaces separated by a layer of lubricant of this composition led to similar results. The separating force is less, the greater the lubricating capacity, and also shows a minimum as a function of the surfactant concentration at the level of saturation of the adsorption layer. Obviously, the determination of this optimal concentration, which is determined primarily by the nature of the surfactant, not by the nature of the metal, is of very great practical interest for efficient, scientifically well founded selection of compositions for lubricating liquids to be used when metals are worked by pressure and cutting, as well as to increase the activity -- "oiliness" -- of lubricating oils. The lubricating effect, i.e., the

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decrease in the coefficient of external friction, can result identically from the formation of an adsorption layer even in those cases when this layer does not increase the extent of solvation of the moving parts by the surrounding medium, but rather decreases it, for example when typical surfactants, whose molecules are oriented upon adsorption with their polar groups to the solid body, and their hydrocarbon chains to the surrounding medium, are added to water. This "hydrophobizing" orientation, as we have seen, sharply decreases the wetability and hydration of the surface by water, therefore having no noticeable dispersing influence. The decrease in friction in this case results from the adsorption layers themselves, the rather long hydrocarbon chains of which create, according to Hardy, a sort of "furriness" of the surfaces which they cover.

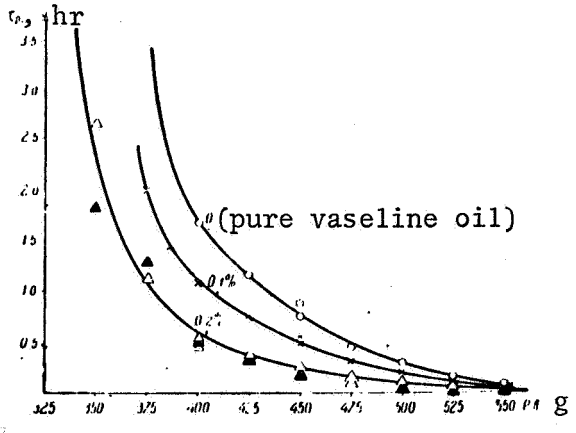

Figure 7. Flow Time to Rupture τ_p As a Function of Load P for Strips of Lead Wire: 0, In pure vaseline oil; 0.1%, 0.2%, In these solutions of stearic acid in vaseline oil. Solid and hollow triangles correspond to two series of experiments.

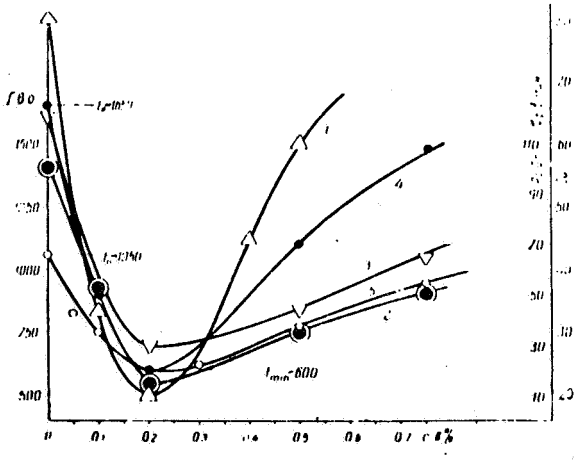

Figure 8. Curves of the Correspondence of the Dependences: a) Of flow time to rupture τ_p on concentration c of stearic acid in vaseline oil: 1, For copper (where P = 1340 g); 2, For lead (P = 300 g); 3, For tin (P = 250 g) and b) Of force of static friction F steel/lead at normal pressure p = 44 kg/cm^2 on concentration c of surfactant in vaseline oil; 4, For stearic acid; 5, For cetyl alcohol.

In the phenomena of facilitation of dispersion, stabilization and particularly the collector effect of reagents during flotation which we have investigated earlier [6, 7], chemical binding of the polar groups of surfactant molecules in the adsorption layer on the surface atoms of the metal can considerably reinforce the effect, strengthening normal orientation of the molecules. During this effect, a gradual transition from the Langmuir bond of the polar groups to the surface by secondary valances to formation in /545

the adsorption layer of definite chemical compounds of a saline nature is noted, for example, during the adsorption of fatty acids, as well as sulfur-containing organic compounds. In this case, the reaction may be purely superficial, limited to the formation of a chemically bonded adsorption monolayer, or may be three-dimensional, in which case the adsorbing surface is covered by a thin crust of the new compound. This case is used in the very interesting experimental investigations of I. V. Grebenshchikov (State Optical Institute in Leningrad), who developed chemical methods for polishing glass and metals. The essence of these methods consists of the formation on the surface of the solid to be polished of new surface compounds in the form of a thin, soft skin, under the influence of a special lubricant paste which contains surfactants (stearic acid) chemically active in the adsorption layer. This surface compound, for example a metal stearate, can be separated from the surface as it is formed by a soft abrasive, to the particles of which it is strongly attracted (also by adsorption); as the new compound is removed, a smooth, shining surface of the metal or glass is revealed. The unique feature of the phenomena investigated by I. V. Grebenshchikov, in contrast to the dispersion facilitating influence of the same adsorbed materials, for example during grinding, is that no mechanical damage such as scratching occurs at all. However, there is no doubt that with fine grinding with a hard, scratchy abrasive such as corundum, both processes occur simultaneously in the medium (solution) -- surface damage of the solid (metal), facilitated by the adsorbed materials, and continuous formation of a film of the new chemical compound which is then broken up, i.e., chemical polishing of the surface. The significance of the purely chemical effect in the adsorption layer in phenomena of dispersion and in the lubricating effect should not be overestimated. This is easily seen from the fact that in our measurements, the addition of cetyl alcohol produces approximately the same facilitation of plastic flow of metals as the addition of stearic acid, although the chemical effect is incomparably sharper in the latter case.

It should also be kept in mind that true polishing is achieved by plastic flow of the solid being polished in the layers near the surface under the influence of high tangential stresses. The flow of the metal during polishing is also facilitated by the extremely high local temperatures formed in the outer layers. The flowing metal fills all irregularities of the surface; according to the concepts of Beilby, confirmed by subsequent X-ray and electronographic investigations, the crystalline lattice near the surface is disrupted; the flowing metal which forms the polished surface is in a glass-like amorphous state. This is facilitated by the local increase in temperature which is developed during polishing. This sort of polishing occurs particularly clearly when the surface of a comparatively soft metal (lead, zinc, copper) is smoothed by a steel polisher; with sufficiently high pressure, the soft metal adheres firmly to the steel surface and flows under the influence of high tangential stresses resulting from this adherence. This true (mechanical) polishing should accompany all forms of cutting (for example grinding) as well as processes of chemical polishing with "GOI pastes" as used by I. V. Grebenshchikov. In all of these cases, the influence of the surface active agents can be felt in the accelerated plastic flow of the metal under the influence of the formation of adsorption layers which we discovered.

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Long ago, the late L. G. Gurvich (Baku), a talented investigator in the area of application of physical chemistry to the problems of oil refining, showed [8] that when lead shot is agitated in nonpolar kerosene, the quantity of "peptized" metal, i.e., the quantity which enters the colloidal-dispersed solution, increases sharply when small quantities of oleic acid, a surface active agent, are added. This phenomenon is closely related to the adsorption reduction in hardness; however, since it consists of fine surface wear in the presence of an active ingredient which interacts chemically with the metal, the process results to a considerable extent from the formation of the metal oleate, as in chemical polishing as described by Grebenshchikov.

When metals are worked by pressure (rolling, drawing), the effect of the lubricating liquids is usually looked upon as a purely external effect, consisting of a reduction of the energy expended in friction. We now see that actually the role of lubricants, primarily their surface active components, includes a considerable amount of facilitation of plastic deformation of the metal being worked due to "internal lubrication." This reduction in the work expended for plastic deformation, together with the reduction of the work required to remove chips -- external dispersion -- is of great significance in the cutting of metals as well.

Basic Conclusions

1. An investigation of plastic flow of specimens of lead, tin and copper (wire and plates) with a cross sectional area of 0.1-1 mm^2 during application of tension by various constant loads in a nonpolar liquid (vaseline oil) and in solutions of surface active agents in the vaseline oil has shown that the flow rate of the metals without rupture increases under the influence of adsorption of surfactants introduced to the nonpolar medium, in which the deformation is performed. Rupture is also facilitated, i.e. the flow time to rupture is /547
decreased with constant force or the force required for rupture is decreased with constant time. For lead, furthermore, a sharp drop in the critical elongation at rupture was noted under the influence of the surfactants added to the nonpolar medium.

2. The form of the dependence of flow time to rupture and other characteristics of plastic flow on the concentration of the surfactant introduced to the nonpolar medium was determined. The correspondence of these dependences with the adsorption isotherm of the surface active agent by the metal from the nonpolar medium was indicated: the greatest effect of facilitation of plastic flow (decrease in time of flow to rupture by a factor of 4-10 upon addition of 0.2% stearic acid, by a factor of 30-60 upon addition of 0.001% cerotinic acid to vaseline oil) corresponds to complete saturation of a monomolecular adsorption layer with the surface active agent on the metal surface. Further increases in the adsorption weaken the effect once more. The effect increases with elongation of the hydrocarbon chain of the surfactant molecule, i.e., as its surface activity increases according to Traub's rule. A reduction in the concentration c_m required to produce the greatest effect was also noted in this case (see table above).

This effect of surface active agents on the flow of metal has not yet been completely explained. However, it can be assumed that it is related on the one hand with facilitation of the beginning of plastic deformation at the surface as a result of adsorption by this surface of polar molecules, and on the other hand with the penetration of adsorption layers and the solvate shells with which they are connected into the depth of the metal along intercrystalline boundaries and slip planes within the crystallites. This would correspond to "internal lubrication," that is, facilitation of plastic flow of the internal portions of the metal, similar to external lubrication.

The greatest, highly expressed effects of the action of the additives should correspond to saturation of a monomolecular layer, i.e., to volumetric concentrations of the surface active agents in equilibrium with a monolayer. This layer also corresponds to the greatest thickness of the solvate shell of the hydrocarbon medium (oil) bonded by the adsorption layer.

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